Intermediate temperature SOFC – a promise for the 21st century

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Abstract

World-wide a number of activities are concerned with the optimisation and development of cell materials and microstructures with the aim of reducing the solid oxide fuel cell (SOFC) operating temperature. Advantages for reduced operating temperatures are considered to be longer life time and reduced costs of the total system. Conventional zirconia based electrolyte cells with highly optimised electrodes have produced 500 mA/cm^2 at 700 mV and 800°C. At a similar temperature and cell potential, small scale, co-fired, electrode supported thin-electrolyte cells have produced 700 mA/cm^2. For SOFC operation at temperatures below 750°C the conventional 8 mol% Y_2O_3–ZrO_2 electrolyte is replaced with either $Ce_{0.9}Gd_{0.1}O_{1.95}$ (10GCO) or $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ (LSGM) electrolytes. Up-scaled 10×10 cm^2 or 12 cm circular 10GCO and LSGM cells have been manufactured and the initial results of cell tests are very promising. © 1998 Elsevier Science S.A.

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1. Introduction

A solid oxide fuel cell (SOFC) consists of a dense zirconia membrane and porous electrodes (Fig. 1). The anode is a Ni-zirconia cermet, whereas the cathode is mostly a Sr-doped lanthanum manganate. At the standard operating temperature of SOFC of 1000°C, direct internal reforming (DIR) of natural gas and other gaseous hydro-carbons directly takes place on the anode structure of the cell. In addition, carbon monoxide is a fuel, not an electro-catalyst poison, for SOFC, in contrast to its behaviour for some low temperature fuel cells. In order to obtain realistic power generating devices, cells are series connected into stacks and developments in SOFC are currently concentrating on tubular stack concepts without metallic components and flat plate concepts with metallic separator plates. Likely entry markets for SOFC are: (1) distributed cogeneration (several 100 kWe to several MWe) with the option of SOFC being a topping cycle in a combined system with a gas turbine and (2) micro combined heat and power (CHP).

2. Operating temperature regimes

From the point of efficiency, state-of-the-art SOFC systems are normally operated in the temperature regime of 850–1000°C. Primary drivers for lowering the operating temperature of SOFCs towards or below 850°C (without losing the DIR characteristics) are: (1) to get an optimum trade-off between performance and life time of the stack and (2) to reduce the overall system cost. In Fig. 2 possible market applications for SOFCs and other fuel cell types are given vs. the operating temperature range of the different fuel cell types. In this diagram different product/market combinations can be distinguished and the need for lowering the operating temperature, i.e. optimising the balance between performance and life time of the stack, is strongly dependent on the stack concept (product) and the application (market). The scenarios envisaged for SOFC are: (1) an operating regime at relatively high temperatures (850–1000°C), e.g. for commercial and industrial cogeneration with or without a combination of a gas turbine (GT), (2) an intermediate temperature regime (650–750°C, e.g. micro CHP application) for SOFC with use of commercially available, cost effective ferritic steels [1] in the stack/system and (3) potential use of SOFC in mobile applications [2] at high
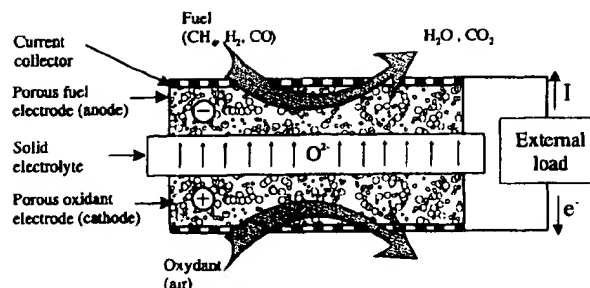
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Fig. 1. Schematic picture of the operating principles of an SOFC. Note the direct internal reforming of CH_4 on the anode electrode.

or intermediate temperatures down to 550°C, depending on the nature of the transport application.

3. Conventional planar cells with reduced temperature operation

The optimisation of electrode materials for the conventional high temperature cells, incorporating yttria stabilised zirconia (YSZ) electrolytes has been ongoing for a number of years. At 950°C, typical single cell performances, in Al_2O_3 cell housings with platinum current collectors and humidified H_2 as fuel and air as the oxidant are in excess of 1 A/cm^2 at 700 mV. Work regarding electrode optimisation has been focused on the development of cathode materials for use in air and the development of anode materials for long term stability under hydrogen as well as under methane/steam mixtures. Activities are concentrating on the development of so called 'biporous layer' electrodes (Fig. 3) [3]. In such a biporous layer electrode the layer adjacent to the electrolyte is called the electrochemically active layer and consists of a mixture of electrolyte and electrode particles showing conductivity of electrons and
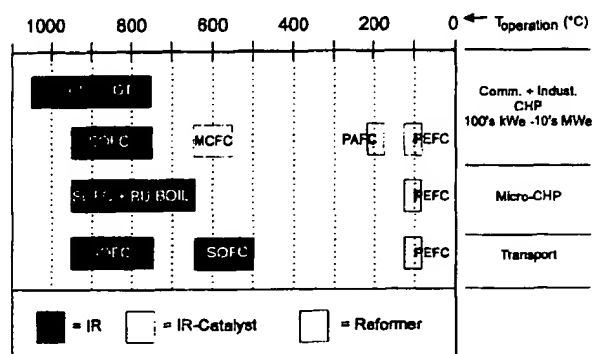

Fig. 2. Possible market applications of SOFCs and other fuel cell types vs. the current or envisaged operating temperature regime. Also indicated is the capability of direct internal reforming of CH_4 on the anode. For SOFC operation at temperatures below 650°C, direct reforming of methanol has been envisaged. For molten carbonate fuel cells (MCFC) direct internal reforming requires the use of additional Ni catalyst in the anode compartment. For phosphoric acid (PAFC) and polymer electrolyte fuel cells (PEFC) external reformers are required. GT, gas turbine; BU/BOIL, conventional burner/boiler system.
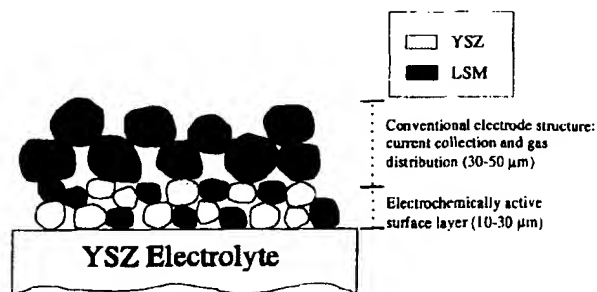

Fig. 3. Schematic picture of a biporous layer electrode, which in this case is a cathode layer.

oxygen vacancies. The second layer on top of the electrochemically active layer consists of the standard cathode material. This layer is primarily for current collection and gas distribution. In addition, the use of alternative dopants for zirconia, e.g. scandium replacing yttrium is being considered.

The performance of conventional high temperature cells, with highly optimised electrode structures has been evaluated at operation temperatures of between 750 and 950°C. Fig. 4 shows that the conventional type cell yields a current density of around 600 mA/cm^2 at 700 mV at 850°C with 3% fuel utilisation and about 300 mA/cm^2 at conditions of 50% fuel utilisation. As a result of the continuing improvement in the performance of SOFC electrodes, it now seems possible to run conventional self-supported YSZ electrolyte cells in planar stacks with metallic separator plates at temperatures between 850 and 950°C and obtain acceptable current densities [4].

4. Alternative cell concepts and manufacturing routes

As the operation temperature is reduced, the ohmic loss of the electrolyte can become very considerable. A number of groups within the SOFC community are therefore working on the development of alternative flat-plate cell concepts in which the thickness of the conventional YSZ electrolyte is reduced to around 20–40 μm. At these thicknesses it is considered [1] that self supporting zirconia electrolytes can
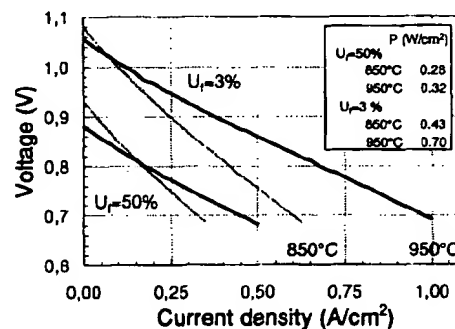

Fig. 4. *I–V* characteristics typical of operating a conventional high temperature cell at temperatures of 850 and 950°C. Fuel utilisation at 50% by simulated gas mixture.

Table 1

Power densities measured from cells manufactured by alternative routes, using electrode supported structures and/or co-firing steps

	Electrolyte (μm)	Sintering steps	P_{max}, 800°C (W/cm^2)	Remarks
University of California [5]	10	3	2.0	Small circular samples 3 cm^2, anode supported
Research Centre Jülich [6]	15	3	0.4	2-cell stack (10 × 10 cm^2), anode supported
Allied Signal [7]	5-10	2	0.65	2-cell stack (10 × 10 cm^2), anode supported, co-fired
University of Utah [8]	10	2	0.5	4-cell stack (5 × 5 cm^2); anode supported, co-fired
Netherlands Energy Research Foundation ECN	30	1	0.6	Small circular samples 3 cm^2, integrated cell structure made by co-firing

no longer be used. Therefore ceramic cells with alternative, high oxygen ion conducting electrolytes and/or with electrode supported thin electrolytes are being developed. These developments are particularly important for use in flat plate SOFC reactors. In Table 1 examples of cell testing results for cells manufactured by alternative routes [5–8] are presented.

5. Alternative cell materials

Alternative cell materials are being considered in order to drive stack operation temperatures down to the point where the expensive high Cr alloys currently used for the metallic parts of planar SOFC stacks can be replaced with cheap ferritic stainless steels. $Ce_{0.9}Gd_{0.1}O_{1.95}$ (10GCO) electrolyte cells have been under development now for a number of years [9]. It has been demonstrated that 5 × 5 cm^2 cells, with 115 μm thick 10GCO electrolytes, $La_{0.6}Sr_{0.4}Fe_{0.8}$-$Co_{0.2}O_3$ (LSCF) cathodes and conventional type anodes can deliver maximum power densities in excess of 200 mW/cm^2 at temperatures as low as 600°C. Operating such cells at 700°C results in maximum power densities of around 500 mW/cm^2. Also, up-scaling of cell dimensions and incorporating cells in the designs of international stack developers has been shown. Fig. 5 shows the performance of
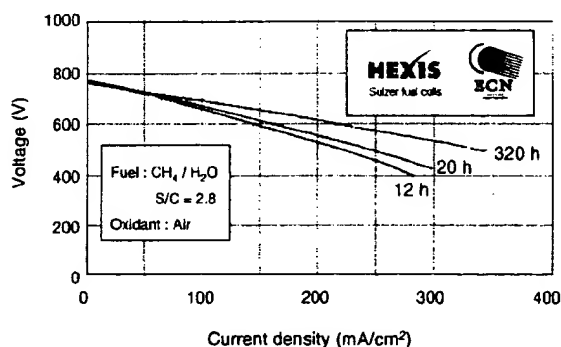

Fig. 5. *I–V* characteristics as a function of operation time of a 150 μm thick. $Ce_{0.9}Gd_{0.1}O_{1.95}$ electrolyte and $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ cathode cell at 700°C operated on reformed natural gas with Sulzer Hexis current collectors. Note, the low open cell voltage due to the electrical short circuiting through the electrolyte and in part to the presence of CH$_4$ on the anode side.

10GCO cells in the Sulzer HEXIS concept at 700°C as a function of operation time. Fig. 6 shows examples of up-scaled, 12 cm diameter 10GCO electrolyte cells manufactured at ECN. In order to reduce the risk of cracking during stack build-up and during reduction of the anode, these cells currently have electrolyte thicknesses in the region of 200–220 μm.

It is well known that the disadvantage of using of the ceria based electrolytes is the relatively small width of the electrolytic domain boundary. Arguments have been made to show that when operated close to maximum power densities, the loss of efficiency due to reduction of the ceria electrolyte is marginal [10]. There remains the fact however, that under open circuit conditions there is a very significant electronic leakage current resulting both in lattice expansion of the electrolyte and fuel utilisation. One possible solution to this problem may be the use of (La,Sr)(Mg,-Ga)O$_3$ based electrolytes. Reports have shown that certain compositions within this system have some of the highest oxygen ion conductivities ever reported and that the width of the electrolyte domain boundary is sufficiently large to use such electrolytes in SOFC systems [11,12]. Small scale (5 × 5 cm^2) and up-scaled (12 cm diameter) $La_{0.9}Sr_{0.1}$-$Ga_{0.8}Mg_{0.2}O_3$ (LSGM) electrolyte cells are also being evaluated and may become an alternative candidate for the ceria based electrolytes. Fig. 7 shows the results of a test in which the performance of a 5 × 5 cm^2 cell with a 200 μm thick

Fig. 6. Examples of up-scaled, 12 cm diameter $Ce_{0.9}Gd_{0.1}O_{1.95}$ (10GCO) electrolyte cells manufactured at ECN.

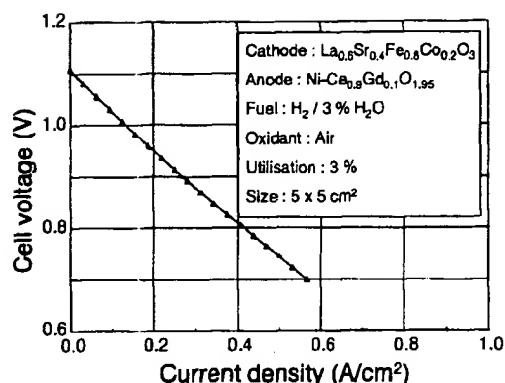Fig. 7. I–V characteristics of a 200 μm thick. $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ electrolyte and $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ cathode cell at 700°C. Note the relatively high open circuit voltage compared with the situation in Fig. 5.

LSGM electrolyte, LSCF cathode and standard type of anode was evaluated at 700°C. The cell was able to be operated at a current density of 550 mA/cm^2 at 700 mV. Further increases in current density are anticipated by optimisation of electrodes.

It should be noted that many challenges and uncertainties remain to be solved with respect to the use of new materials and manufacturing concepts, i.e. (1) chemical stability of new materials, (2) thermo-mechanical behaviour, (3) costs of raw materials and cell manufacturing, (4) performance under realistic stack/system conditions and (5) direct internal reforming characteristics at these lower operating temperatures.

6. Conclusions

It is concluded that the need for intermediate temperature SOFC operation is strongly dependent on the SOFC concept and the envisaged application. Conventional high temperature cells with zirconia based electrolytes and highly optimised electrode structures show an acceptable performance when operated at 800°C and higher. Further improvements of electrochemical performance for state-of-the-art materials at lower temperatures may come from dedicated ceramic processing or 'engineering' of the electrolyte/electrode interface, i.e. the electrochemically active layer and from up-scaling advanced manufacturing concepts for supported thin electrolyte cells. The use of alternative cell materials for operating temperatures between 550 and 750°C with ferritic steel separator plates, looks promising. Up-scaled,

12 cm diameter and 10 × 10 cm^2, $Ce_{0.9}Gd_{0.1}O_{1.95}$ and $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ electrolyte cells are routinely manufactured and the performance of these cells in real stack conditions is being evaluated at present at, e.g. Sulzer HEXIS and Siemens. However, the relatively recent developments in these alternative materials have to compete with currently existing know-how for standard materials which is relying on several tens of years of experience.

Acknowledgements

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